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Abstract
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Keywords
Ames Laboratory, spectroscopy, antiferromagnetic-ferromagnetic, Fermi surface

Disciplines
Atomic, Molecular and Optical Physics | Condensed Matter Physics | Physics

Comments
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Ellipsometric studies of magnetic phase transitions of Fe-Rh alloys

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Spectroscopic ellipsometric measurements of the dielectric functions for Fe-Rh alloys with 48, 50, 52, and 54 at. % Fe concentrations were performed between 25 and 125 °C in the 1–3-eV range. Results show that the band structure of Fe-Rh is not drastically affected as the antiferromagnetic-ferromagnetic phase transition occurs and is less affected than band-structure calculations indicate. Therefore, the large change in the linear term of the electronic specific heat between the antiferromagnetic and ferromagnetic phases can be attributed primarily to a magnetic contribution rather than to a change in the density of electronic states at the Fermi surface.

I. INTRODUCTION

In 1938, when Fallot[1] studied the magnetic properties of the Fe-Rh alloy system, he found that a first-order phase transition from the low-temperature antiferromagnetic (AF) state to the high-temperature ferromagnetic (F) state occurs at a critical temperature T_{crit}, approximately 65 °C, for a nearly equiatomic ordered Fe-Rh alloy. He also reported that this magnetic phase transition can occur at room temperature with an increase of a few atomic percent of the Fe concentration. Since then many detailed studies,[2–16] both theoretical and experimental, have been made.

The crystal structure of the equiatomic alloy $Fe_{0.50}Rh_{0.50}$ is the CsCl type[17,18] with one Rh atom and eight nearest-neighbor Fe atoms at the center and corners of a simple-cubic unit cell, respectively. The chemical lattice parameter, a, is equal to 2.986 Å.[3] At room temperature and normal pressure, $Fe_{0.50}Rh_{0.50}$ is in the AF state. The moment of the Rh atom is close to zero, and the simple-cubic chemical lattice of Fe atoms can be viewed as two interpenetrating fcc magnetic sublattices, giving an antiferromagnetic alloy,[10,19] with a magnetic lattice parameter $a'=2a$ and a moment of $3.3\mu_B$ per Fe atom, as seen in Fig. 1. The AF-F phase transition can occur by changing either the Fe concentration in alloys or the temperature of the material. For the former case, at room temperature when the concentration of Fe is raised from 0.50 to ~0.51–0.52, the transition occurs with moments of $\sim 3.1\mu_B$ and $1.0\mu_B$ on Fe and Rh atoms, respectively, in the F phase. The moment on the Fe atom substituted for a Rh atom is equal to about $2.5\mu_B$.[10,19] For the latter case, the first-order magnetic phase transition takes place in an equiatomic Fe-Rh alloy as the temperature increases from room temperature to a critical temperature (T_{crit}) of ~65 °C.[1,3,10] A second-order phase transition also has been reported.[7] As the temperature further increases to the Curie temperature (T_C) somewhere between 300 and 400 °C, a paramagnetic (P) phase appears in the $Fe_{0.50}Rh_{0.50}$ alloy. The space group for the F and P phases is the CsCl (O_h^1) type, whereas for the AF phase it is the NaCl (O_h^5) type. It has also been observed that at the AF→F transition the volume increases by ~1%, although there is no structural change.[15,16,18]

In order to explain the nature of this first-order transition, Kittel[11] presented an exchange-inversion model in which he suggested that the exchange parameter is assumed to depend upon the lattice constant and to change sign at a certain value of the lattice constant. Unfortunately, this model failed to give a satisfactory interpretation for Kouvel's results[20] in which a large entropy change was observed in the transition region. On the basis of their experimental results, Tu *et al.*[8] suggested another model, in which the change of the band electron entropy is assumed to play the main role in the AF-F transition. They found that the electronic specific heat of ferromagnetic samples is about four times as high as that of antiferromagnetic samples, so that at T_{crit} the Gibbs free energy gained from the electron entropy exceeds the loss of internal energy if the AF-F transition occurs. Later, a more detailed treatment of the nature of the transition was given by Ricodeau and Melville.[21] They pointed out that the changes in the electronic, lattice, and

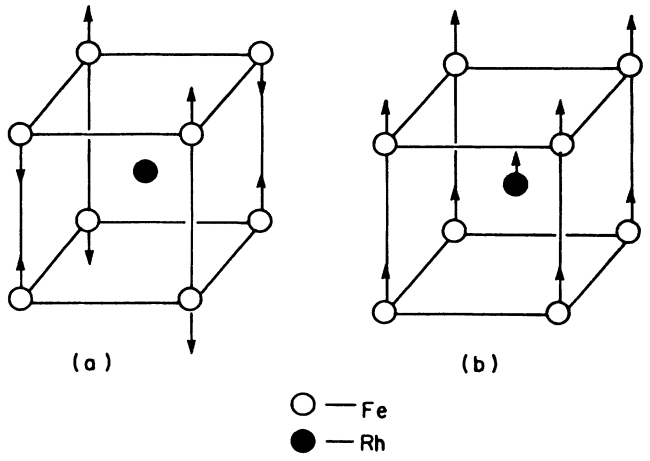

FIG. 1. Magnetic structures of $Fe_{0.5}Rh_{0.5}$ in the (a) AF phase and (b) F phase.

magnetic energies are about equally important for the AF-F transition, and that the change in physical properties at the transition temperature may be due to a change in the electronic density of states at the Fermi level. Specific-heat measurements[8,9,22] supported the idea that a higher density of states at the Fermi level should be associated with the F phase rather than the AF phase. In spite of a long-standing need for a band-structure calculation to aid in the interpretation of this phase transition, such a calculation was carried out only recently.

It was reported[12] that the first band-structure calculation (unpublished) was made by Fletcher using a Korringa-Kohn-Rostoker Green's-function (KKR) method, but his result gave surprisingly almost the same density of states at the Fermi level in both the AF and F phases. In terms of a simple tight-binding model, Khwaja and Nauciel-Bloch[2] dealt with the band structure of the $Fe_{0.50}Rh_{0.50}$ alloy only in the AF phase. Later, Khan[12] carried out a more extensive band-structure calculation using the same method, giving an estimate of the *d* partial densities of states on the Fe and Rh sites in the AF, F, and P phases. But in all these methods, experimental magnetic-moment data were used to fit the calculations and none were self-consistent. Recently two self-consistent calculations were given by Kulikov *et al.*[23] and Koenig,[4] respectively. The former used an augmented-plane-wave method to treat only the P phase. The latter utilized a linear muffin-tin-orbital method combined with the atomic-spheric approximation to calculate the energy bands in all three magnetic phases and gave the electronic specific-heat coefficients in agreement with experiment results. According to Koenig's explanations, the low value of the density of states at the Fermi level for the AF phase is caused by a Slater splitting of the band, due to the doubling of the lattice parameter at the transition. On the basis of Koenig's scheme, Khan *et al.*[5] made further efforts to calculate the dielectric functions of Fe-Rh in all three phases by considering only direct interband transitions, as shown in Fig. 2, although there was a lack of experimental data for verifying the calculations.

Therefore, it is important to make optical measurements to obtain the dielectric functions of Fe-Rh alloys for verifying the results of the band calculations and as an aid to understanding this unique phase transition.

II. SAMPLE PREPARATION AND MEASUREMENT

We made four alloy samples with Fe concentrations of 48, 50, 52, and 54 at. %, respectively. All samples were made from weighed amounts of bulk iron (99.99% pure) and powdered rhodium (99.95% pure) by arc melting in an argon atmosphere. The weight loss during melting did not exceed 0.1%, which gave compositions in agreement with later wet-chemical analysis of sample compositions. Samples then were annealed at 1000 °C in argon in sealed tantalum capsules for ~7 d and cooled slowly to room temperature. The grain size after annealing grew to ~1–4 mm. After heat treatment, lattice parameters were measured by x-ray diffraction at room temperature as shown in Table I. It can be seen that all three samples

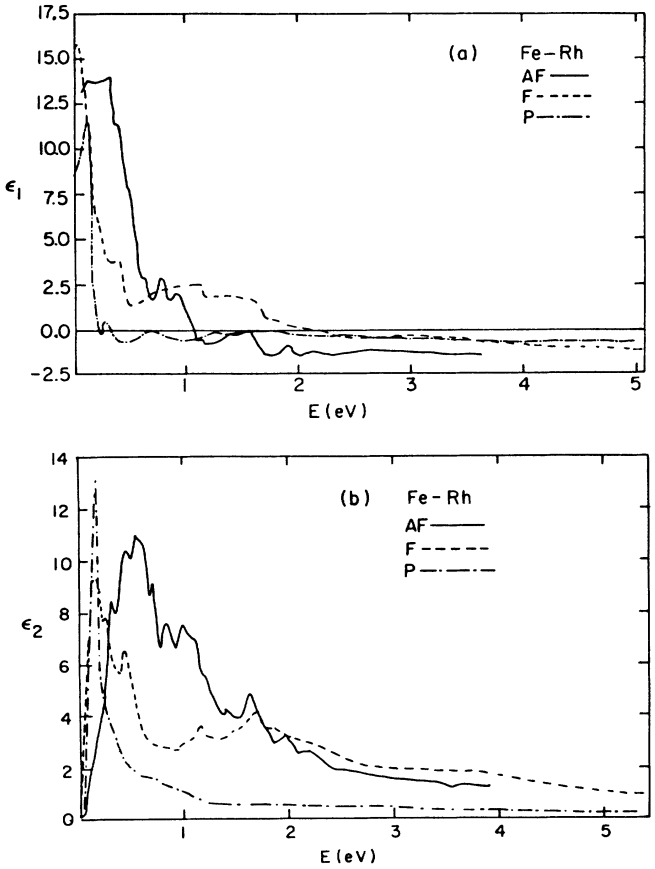

FIG. 2. (a) Calculated real parts of the interband dielectric functions in the three phases of $Fe_{0.5}Rh_{0.5}$ (Ref. 5). (b) Calculated imaginary parts of the interband dielectric functions in the three phases of $Fe_{0.5}Rh_{0.5}$

with Fe concentrations at or above 50 at. % are of a single α phase (bcc), but the sample with 48 at. % Fe has mixed α and γ phases (bcc and fcc). These are in agreement with other authors' observations[3,24] and with the phase diagram shown in Fig. 3.[3] Magnetization measurements were made at room temperature for the samples with 48 and 54 at. % Fe, respectively, which confirmed that the former is antiferromagnetic and the latter is ferromagnetic, in agreement with other authors' results.[10]

Samples were mechanically polished with alumina powders of down to 0.05-μm diameter in liquid and afterwards cleaned by methanol. An ellipsometric technique which has been discussed previously[25,26] was used to determine the dielectric functions. Measurement errors

TABLE I. Lattice parameters of Fe-Rh alloys measured by x-ray diffraction.

(at. %) Fe	Unit cell (±0.0005 Å) (Å) α (bcc)	β (fcc)
48	3.0044	3.7486
50	2.9976	
52	2.9966	
54	2.9944	

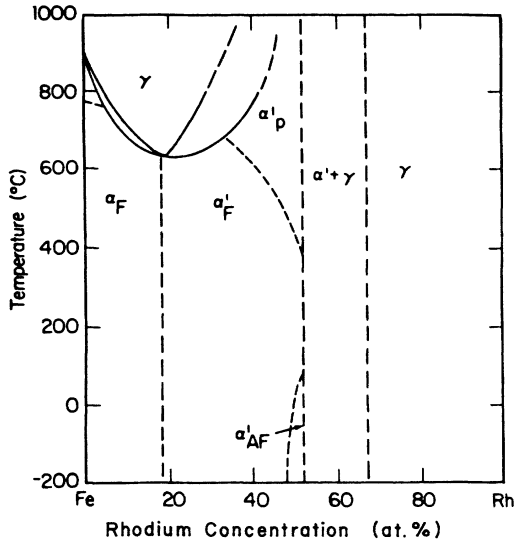

FIG. 3. Approximate phase diagram of the Fe-Rh system (Ref. 3).

did not exceed 1%. All measurements were made in the 1–3-eV region with an energy interval of 0.01 eV and a spectral bandpass of 3.3 nm. The measurements were done within about half an hour after the samples had been polished and cleaned. Since the Fe-Rh surfaces have been shown to be very stable in the atmosphere, the oxidized overlayer on the surface appears to be quite thin. It will exert a small effect on the absolute values of dielectric functions but not on the structures. Its effect can be neglected for our purposes.

III. RESULTS

The dielectric functions of Fe-Rh alloys measured at room temperature for different Fe concentrations are shown in Fig. 4. Although there are changes in the magnitudes with variation of Fe concentration, it is clear that shifts in the positions of the main structures are negligibly small. Changes in both the real and imaginary parts of the dielectric function with composition are almost monotonic, except for the sample with 52 at. % Fe. For every sample, we also measured the dielectric function at different temperatures: 25, 75, 100, and 125 °C. The dielectric functions of our Fe-Rh alloys were very insensitive to temperature, and the curves obtained for each sample at different temperatures are identical to those in Fig. 4 to within 1%. Thus error bars are about as high as the width of the lines. The accuracy of the data is harder to assess, for it depends on surface quality.

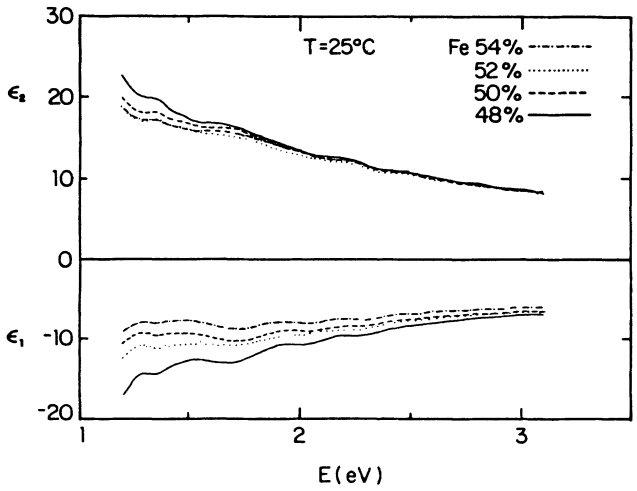

FIG. 4. Complex dielectric functions of Fe-Rh for different Fe concentrations.

The data in the 1–3-eV range consist of two parts: contributions from intraband and interband transitions. To compare quantitatively the results to the calculated curves shown in Fig. 3, the contribution from the free electrons needs to be subtracted from the measured data. Since the Drude parameters for Fe-Rh cannot be measured in our spectral range, we use indirect data to deduce approximate parameters. From the Drude theory,[27] we have

$$\epsilon_2^f = \frac{\omega_p^2 \tau}{\omega(1+\omega^2\tau^2)} = \frac{4\pi\hbar\sigma_0}{E[1+E^2(\tau/\hbar)^2]} , \quad (1)$$

where τ is the relaxation time of the free electrons. τ can be found from the dc conductivity σ_0 and plasma frequency ω_p,

$$\tau = \frac{4\pi\sigma_0}{\omega_p^2} , \quad (2)$$

where

$$\hbar\omega_p = 28.875(Z_M \rho_M / A_M)^{1/2} \text{ eV} . \quad (3)$$

Z_M, ρ_M, and A_M are the number of electrons per molecule, mass density in g/cm^3, and molecular weight, respectively. By using a lattice parameter of 2.99 Å, and two atoms per unit cell and considering only s-p electrons, $Z_M = 3$ and $\hbar\omega_p = 12.46$ eV. But Fe-Rh has a partially filled d band,[4] and counting d electrons as well, $Z_M = 17$ and $\hbar\omega_p = 29.67$ eV. (Electron-energy-loss spectra show a well-resolved peak at 8.5 eV and a very broad peak at 29.5 eV, both representing longitudinal resonances. Because of interband transitions, the 8.5-eV peak may be shifted considerably from the position expected for a free-electron gas.) The dc resistivity of $Fe_{0.5}Rh_{0.5}$, measured by Schinkel *et al.*,[7] at room temperature, is about 130×10^{-6} Ω cm. Therefore, from Eqs. (1)–(3), the free-electron contribution from s-p electrons only is

$$\epsilon_2^f = \frac{57.43}{E[1+(4.6E)^2]} , \quad (4)$$

and for the contribution from the s-p-d electrons,

$$\epsilon_2^f = \frac{57.43}{E[1+(1.93E)^2]} , \quad (5)$$

with E in eV.

After the Drude contribution has been subtracted from

the original data, the remaining interband part of ϵ_2 for the $Fe_{0.50}Rh_{0.50}$ sample is shown in Fig. 5 with a comparison to the calculated curves for the AF and F phases.

To enhance the structures in the spectra and to make a precise determination of their positions, $\partial\epsilon_2/\partial E$ and $\partial^2\epsilon_2/\partial E^2$, the first and the second derivatives of the imaginary part of the complex dielectric functions taken from our corrected data of curve C in Fig. 5, were calculated for each sample. Tabulated coefficients taken from the literature[28,29] were used to compute the derivatives and a least-squares nine-point smoothing method was used to suppress noise in the derivative spectra without distorting the line shape. (Some artifacts from experimental errors or noise are still present in these plots). Spectra of $\partial\epsilon_2/\partial E$ and $\partial^2\epsilon_2/\partial E^2$ are shown in Figs. 6 and 7, respectively. The transition energies at strong structures were decided by $\partial\epsilon_2/\partial E=0$ and $\partial^2\epsilon_2/\partial E^2<0$, and at weak shoulders by $\partial^2\epsilon_2/\partial E^2=0$. These values and those taken from the spectra calculated from the band-structure calculations[5] are listed in Table II. Although beyond 2.5 eV there are also several very weak shoulders, we did not pay serious attention to them.

IV. DISCUSSION AND CONCLUSION

As mentioned above, the most recent band-structure calculations all favor the view that at the AF→F phase transition for Fe-Rh alloys, the large increase in the value of the linear term of the low-temperature specific heat mainly arises from the large difference of the electronic density of states at the Fermi level between those two phases. Based on their computed band-structure results, Khan *et al.*[5] made further calculations on the complex dielectric functions of Fe-Rh in all three phases. Unfortunately, our dielectric function data in Figs. 4–7 are unable to support those calculations.

First, it is clear from magnetic measurements that at room temperature the samples containing 48 and 50 at. % Fe are antiferromagnetic. They should become ferromagnetic when the temperature is raised above the critical temperature, T_{crit}, ~330–350 K. For all our samples, however, we observed no temperature-dependent change of the dielectric functions in the temperature range of 25–125 °C (300–400 K).

Second, at room temperature the rhodium-rich and iron-rich samples are definitely antiferromagnetic and ferromagnetic, respectively. As seen from Figs. 4–7 and Table II, although there are changes in the absolute values of dielectric functions with Fe content varying from 48 to 54 at. %, the contour of the curves and the positions of the major features of the spectra have not been significantly affected.

The measured position of the main "peak" the broad structure around 1.7 eV in all samples, is in good agreement with the calculated value of 1.686 eV for the ferromagnetic state,[5] although there are a few weaker structures which, especially around 2.2 eV, are in agreement with the calculated spectra for the antiferromagnetic phase. (See Table II.) The 1.7-eV peak should vanish or

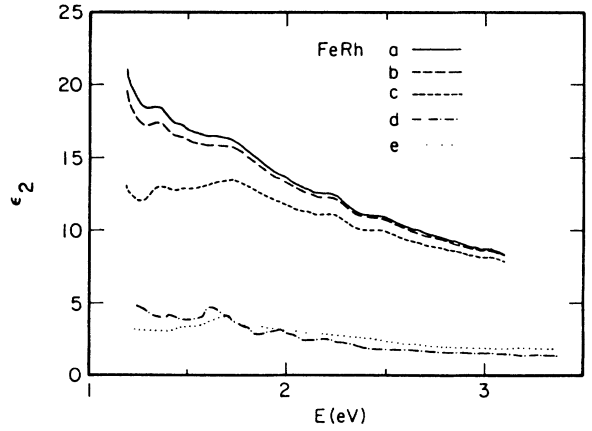

FIG. 5. ϵ_2 spectra of the $Fe_{0.5}Rh_{0.5}$ alloy. (a) Original data, (b) corrected data after subtracting the Drude contribution from *s-p* electrons, (c) corrected data after subtracting the Drude contribution from *s-p-d* electrons, (d) calculated spectrum for the AF phase (Ref. 5), and (e) Calculated spectrum for the F phase (Ref. 5).

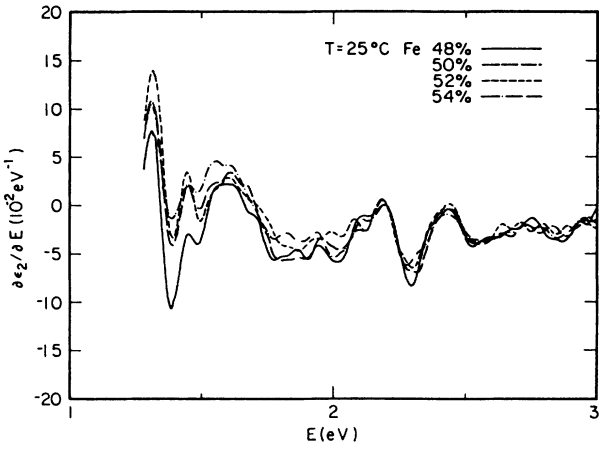

FIG. 6. First derivative ϵ_2 spectra of Fe-Rh alloys for different Fe concentrations.

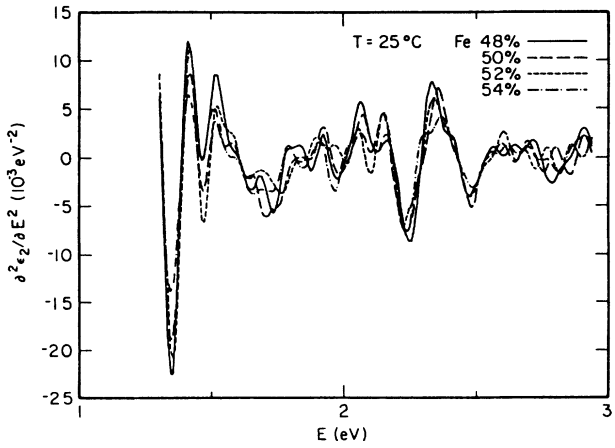

FIG. 7. Second derivative ϵ_2 spectra of Fe-Rh alloys for different Fe concentrations.

TABLE II. Comparison between the theoretical calculations and the experimental data of Fe-Rh alloys at absorption peak positions in the 1–3-eV range.

	Calculated values (eV)		Experimental values (±0.005 eV) for concentration of Fe (at. %)			
P	F	AF	48 (AF)	50 (AF-F)	52 (F)	54 (F)
	1.142[a]					
		1.406[b]	1.347[c]	1.366[c]	1.366[c]	1.366[c]
	1.496[a]			1.486[c]	1.476[c]	
		1.605[a]				
	1.686[a]		1.667[c]	1.706[c]	1.717[c]	1.695[c]
	1.850[a]		1.856[d]	1.867[d]		1.817[d]
		1.968[b]	1.945[d]	1.956[d]	1.996[d]	1.935[d]
		2.194[b]	2.207[c]	2.207[c]	2.196[c]	2.196[c]
		2.604[b]	2.435[d]	2.435[d]	2.435[d]	2.426[d]

[a]Data from Ref. 5.
[b]Data from digitized curves in the figures of Ref. 5.
[c]From zero of the first energy derivative of curve C in Fig. 5.
[d]From zero of the second energy derivative of curve C in Fig. 5.

shift to lower energy in the antiferromagnetic phase, according to the calculated spectra, but we found it present identically in the spectra of both phases.

Upon changing phase, AF→F, the calculated interband ϵ_2 loses oscillator strength in the 0.25–1.75-eV region, and gains a smaller amount in the region from 2.75 to 4 eV [Fig. 2(b)]. In addition, the principal structure in the region of our measurements, a peak at 1.6 eV, weakens and shifts to about 1.7 eV. There are other weaker structures which change, but in view of the fact that the calculated spectra were not broadened in Fig. 2(b), the actual broadening, quite large in transition metals,[30] will remove most of them. Moreover, the calculated energies of the structures will be in error due to the effect of the neglected real part of the self-energy, but the shift caused by the phase change may be reliable.

Looking at Fig. 8, we see no such effect as the Fe content increases. In this figure, the Drude contribution has been subtracted using Drude parameters with the *d* electrons of stoichiometric Fe-Rh for all four samples. The changes in τ cannot be extracted reliably from the resistivity data in Ref. 7, but they appear to be no more than 15% for nonstoichiometric samples. No peaks appear to shift, which is more easily determined from plots of the energy derivative of ϵ_2. It thus appears that the calculated dielectric functions are not in quantitative agreement with our data, and even qualitative agreement is not really found. Measurements further into the infrared would be useful.

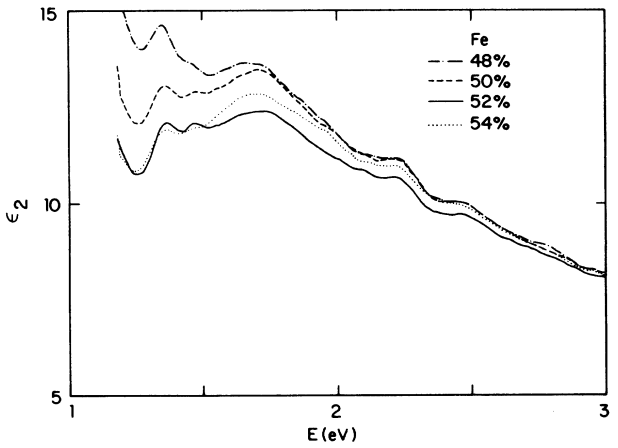

FIG. 8. Imaginary parts of dielectric functions of Fe-Rh for different Fe concentrations after subtracting the Drude contribution from the *s-p-d* electrons.

To explain the divergence between our experimental results and the calculations by Khan *et al.*, we have to go back to the original discussion of this interesting magnetic phase transition problem, for this difference plays a role in the magnetic phase transition.

When Tu *et al.*[8] studied the first-order AF-F phase transition by measuring the low-temperature specific heat of the Fe(Rh,Pd) system, they suggested that the large entropy change at T_{crit} comes probably from the contribution of the electron gas at the Fermi surface. They further assumed that the electron entropy S for Fe-Rh alloys changes linearly with temperature, i.e., $S=\gamma T$, where γ is the coefficient of the linear term in the specific heat and is proportional to the density of states at the Fermi surface. Thus, they derived an expression for T_{crit} in terms of γ in both the AF and F states,

$$T_{\text{crit}}^2=\frac{|U_{\text{AF}}^0|-|U_{\text{F}}^0|}{\gamma_{\text{F}}-\gamma_{\text{AF}}}\ , \tag{6}$$

where U_{AF}^0 and U_{F}^0 are the ground-state energies in the AF and F phases, respectively.

Since the measurements of γ for the Fe-Rh system were never made on samples which had identical compositions, Ponomarev[31] suspected that the change of γ may have a strong dependence on composition. He tried to determine the change in γ for the same sample by measuring the dependence of the critical magnetic field on temperature. But there was no evidence that the relationship $S=\gamma T$, supposed by Tu *et al.* and used in

Ponomarev's method, would be valid beyond the low-temperature range.

Fogarassy *et al.*[32] pointed out that Eq. (6) derived by Tu *et al.* may not be true. The addition of a few percent Pd to Fe-Rh alloys decreases the transition temperature. From Eq. (6) one would expect that

$$(\gamma_F-\gamma_{AF})_{Fe\text{-}Rh(Pd)}>(\gamma_F-\gamma_{AF})_{Fe\text{-}Rh} . \quad (7)$$

Results,[32] however, contradict this expectation. They also found that adding a few percent Ir to Fe-Rh alloys increases the values of γ_{AF} by a factor of 10–20. The measured γ_{AF} values in the Fe-Rh(Ir) system are too large to be interpreted as arising from the electron specific heat alone. They raised the suspicion that this large increase in the specific heat may come from a magnetic contribution. To check this possibility, they made a further measurement of the specific heat of an Fe-Rh alloy with an antiferromagnetic phase containing 5 at. % Ir in the presence of a 20 KOe magnetic field and found that the measured γ_{AF} increases by $\sim 15\%$. But for the ferromagnetic $Fe_{0.52}Rh_{0.48}$ alloy, they did not see such an influence of the magnetic field.

The phenomenon of a drastic change of the measured γ with composition was also observed in other alloy systems, Cu-Ni(Al), V-Fe(Al), Fe-Al, and Mn-Ni, etc., by Beck and his co-workers.[33–36] They all believed that the large increase of γ at a certain critical composition is probably attributable to the magnetic contribution, rather than to the electronic specific heat alone. Therefore, the measured γ consists of two parts,

$$\gamma=\gamma_e+\gamma_M , \quad (8)$$

where γ_e and γ_M are the contributions from the electronic and magnetic parts, respectively. Although the magnetic effect on the specific heat has been well recognized and discussed by them, a direct measurement of γ_M has not been made since then.

Although there were serious objections to his proposals, it was Overhauser[37] who first gave a theoretical result from which a low-temperature linear term, γ_M, with a magnetic origin was obtained. This theory postulated that a large number of spins are located in a near-zero field as a result of the presence of static spin waves in an antiferromagnetic structure. On the basis of the Ising model, Marshall[38] proposed a modification of Overhauser's idea and found a magnetic term in the specific heat which was linear in T at low temperatures. Marshall's model is assumed to fit a dilute system. But Beck *et al.*[33–36] suggested that in principle it can be effective in concentrated alloys. In this theory, the character of the change in γ_{AF} depends strongly on $P(T,H)$, a distribution function of the effective magnetic field H. The actual form of $P(T,H)$ may not be important, but if $P(T,H)$ presumably has a local minimum at $H=0$ one could expect an increase of γ_{AF} in the presence of an effective magnetic field.

It appears that Marshall's theory provides a reasonable physical basis for explaining the large change of γ for the Fe-Rh system as the AF-F transition occurs. Although the total effective magnetic field acting on the central spin in an antiferromagnetic phase may not be exactly canceled to zero, this field indeed reaches its minimum. (See Fig. 1.) On the contrary, a maximum value of the effective field will be achieved in the ferromagnetic phase since all spins are aligned. The difference of the effective magnetic field between these two phases could be so large that it is the origin of the increase in the specific heat of Fe-Rh alloys.

Now we look back at Koenig's calculations.[4] He used a linear muffin-tin-orbital (LMTO) method within an atomic sphere approximation to treat the Fe-Rh system by assuming that the two atomic spheres for iron and rhodium have the same radius R_a. First, he managed to compute the band structure and got the potential in the P phase. Then, a constant value was added to this starting potential of the P phase in trying to fit approximately the experimental data of the magnetic moments of the F phase. Next he calculated this new potential again in iteration and obtained finally the band structure of the F phase. The same procedures were taken to treat the AF phase. But instead of using two atoms per cell as in the P and F phases, four atoms per cell, i.e., a doubled lattice parameter, were used in the AF phase. The calculations of the dielectric function by Khan *et al.*[5] were based on Koenig's results. However, by comparison to the spectra in Figs. 5–8 and the data in Table II, we can say that there is some agreement between the calculated and experimental spectra only for the ferromagnetic phase, especially in the strongest structure, the peak in ϵ_2 near 1.7 eV. Furthermore, it seems to us that our ellipsometric data are not in favor of the idea that the band structure of the Fe-Rh alloy is drastically affected at the AF-F transition. Therefore, we would like to suggest that improved band-structure calculations be carried out on the Fe-Rh system, including nonstoichiometric Fe-Rh, in order to obtain a better understanding of the physical properties of Fe-Rh alloys.

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